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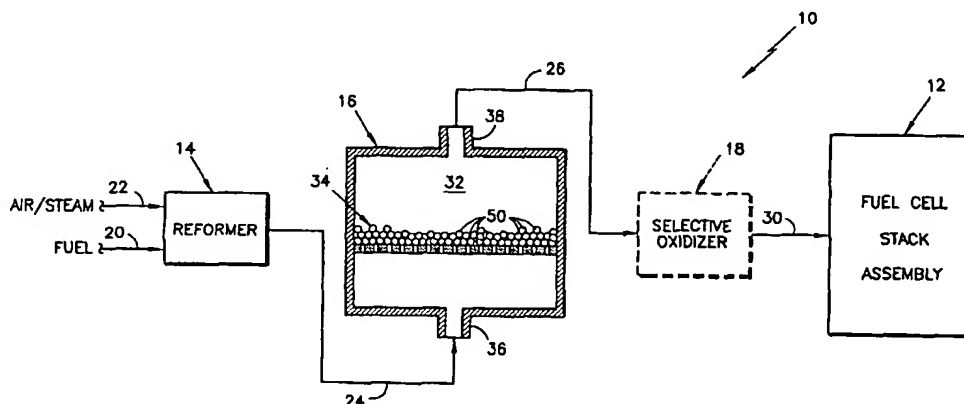
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(54) Title: SHIFT CONVERSION ON HAVING IMPROVED CATALYST COMPOSITION



(57) Abstract: A shift converter (16) in a fuel processing subsystem (14, 16, 18) for a fuel cell (12) uses an improved catalyst composition (50) to reduce the amount of carbon monoxide in a process gas for the fuel cell (12). The catalyst composition (50) is a noble metal catalyst having a promoted support of mixed metal oxide, including at least both ceria and zirconia. Cerium is present in the range of 30 to 50 mole%, and zirconium is present in the range of 70 to 50 mole%. Additional metal oxides may also be present. Use of the catalyst composition (50) obviates the requirement for prior reducing of catalysts, and minimizes the need to protect the catalyst from oxygen during operation and/or shutdown.

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SHIFT CONVERSION ON HAVING IMPROVED CATALYST COMPOSITION

Technical Field

This invention relates to hydrocarbon fuel processing, and more particularly to
5 an improved shift converter and the catalysts used therein. More particularly still, the
invention relates to improved catalyst compositions in, and used in, shift converters
for processing hydrogen-rich gas streams, as for use in fuel cells.

Background Art

Fuel cell power plants that utilize a fuel cell stack for producing electricity
10 from a hydrocarbon fuel are well known. In order for the hydrocarbon fuel to be
useful in the fuel cell stack's operation, it must first be converted to a hydrogen-rich
stream. Hydrocarbon fuels that are used by the fuel cell stack pass through a
reforming process to create a process gas having an increased hydrogen content that is
introduced into the fuel cell stack. The resultant process gas contains, primarily,
15 water, hydrogen, carbon dioxide, and carbon monoxide. The process gas has about
10% carbon monoxide (CO) upon exit from the reformer.

Anode electrodes, which form part of the fuel cell stack, can be "poisoned" by
a high level of carbon monoxide. Thus, it is necessary to reduce the level of CO in the
process gas, prior to flowing the process gas to the fuel cell stack. This is typically
20 done by passing the process gas through a shift converter, and possibly additional
reactors, such as a selective oxidizer, prior to flowing the process gas to the fuel cell
stack. The shift converter also increases the yield of hydrogen in the process gas.

Shift converters for reducing the CO content of process gas are well known,
and typically comprise a chamber having an inlet for entry of the process gas into the
25 chamber, an outlet downstream of the inlet for exit of effluent from the chamber, and
a catalytic reaction zone between the inlet and the outlet. The catalytic reaction zone
typically contains a catalyst, or catalyst composition, for converting at least a portion
of the carbon monoxide in the process gas into carbon dioxide. In operation a shift
converter carries out an exothermic shift conversion reaction represented by the
30 following equation:



The reaction (1) between the CO and water concurrently reduces the CO content and increases the CO₂ and H₂ content of the process gas. The generation of additional hydrogen from this reaction is advantageous to the power plant inasmuch as hydrogen is consumed at the fuel cell anode to produce power. A discussion of one such shift

5 converter is contained in PCT Application US97/08334 for "Shift Converter", published on 27 November 1997 as WO 97/44123. In the shift converter of that application, a catalyst bed contains a catalyst composition of copper and zinc oxide, or copper, zinc oxide, and alumina. Such catalyst composition is further disclosed in U. S. Patent 4,308,176 to Kristiansen, and has been used for a number of years to

10 promote the shift reaction in the shift converters associated with fuel cell power plants. However, reactors using these catalyst compositions have the limitation that they must be purged with a flow of hydrogen to initially reduce them, and steps must be taken subsequent to operation to prevent significant oxidation or exposure to oxygen. In fact, the required reaction does not work, or occur, unless the catalyst is

15 reduced. Exposure of these catalyst compositions to oxygen is, or may be, detrimental to the catalyst. This is because the catalyst is self-heating in the presence of oxygen, and it can easily heat itself to the point where catalyst particles will sinter, and thus lose surface area and decrease activity. This need to provide a reducing atmosphere and to minimize the possibility of oxygen leaks to the catalyst with a special

20 shutdown purge and the maintenance of an inert atmosphere during shutdown, results in additional hardware and process control considerations that add to the complexity and cost of the fuel cell power plant system, particularly with regard to the shift converter.

Recent studies show that cerium oxide, or "ceria" (CeO₂), can be used in

25 combination with a noble metal to promote the shift reaction and to eliminate the requirement that the catalyst be reduced. The combination of ceria and platinum provide a catalyst that is more oxygen tolerant than the prior catalysts. However, such ceria-promoted platinum catalysts have not demonstrated sufficient activity for the shift reaction to be useful in a reactor of a reasonable size. Rather, an unreasonably

30 large catalyst bed would be required, particularly for mobile fuel cell power plants. Moreover, water levels typical of water-gas shift reactions may promote sintering of the ceria support.

The present invention can provide a shift converter having an improved catalyst composition for efficiently converting carbon monoxide to carbon dioxide and hydrogen using a water-gas shift reaction without the need for special catalyst preconditioning. It can further provide and use an improved catalyst composition
5 having increased activity in a shift conversion reactor for converting carbon monoxide to carbon dioxide and hydrogen using a water-gas-shift reaction without the need to protect the catalyst from exposure to air. It can further provide and use an improved catalyst composition providing improved activity and durability over existing noble metal catalysts for the water-gas-shift reaction.

10

Disclosure of Invention

A shift converter for reducing the amount of carbon monoxide in a process gas, as for a fuel cell power plant, uses an improved catalyst composition in accordance with the invention. The shift converter includes an inlet for entry of the process gas, an outlet downstream of the inlet for exit of effluent from the chamber,
15 and a catalytic reaction zone between the inlet and outlet. The catalyst composition of the invention resides in the catalytic reaction zone of the shift reactor and is active to convert at least a portion of the carbon monoxide and water in the process gas into carbon dioxide and hydrogen. The operation of the shift reactor with the improved catalyst composition obviates the prior requirements for pre-reducing the catalyst,
20 providing a special post-shutdown purge, and maintaining an inert atmosphere during shutdown.

The improved catalyst composition used in the shift converter comprises a noble metal catalyst having a promoted support, which promoted support comprises a mixed metal oxide of at least cerium oxide (ceria) and zirconium oxide (zirconia).
25 The inclusion of the zirconia with the ceria promoter increases the number of oxygen vacancies, and thus the composition's activity. Moreover, the zirconia increases the resistance of ceria to sintering, thereby improving the durability of the catalyst composition. The mixed metal oxides, in addition to the ceria and zirconia, may include a third metal oxide, selected from the group consisting of praseodymium
30 oxide, lanthanum oxide, neodymium oxide, and hafnium oxide, to form a ternary mix of the metal oxides. Additionally, alumina may be added to the catalyst composition, particularly if the latter is in the powder form, to improve its suitability for washcoating onto a supporting substrate.

The noble metal catalyst on the promoted support is selected from the metals of groups VIIb, VIII, and Ib of the second and third transition series of the periodic table, with platinum, palladium, rhodium, and gold being generally preferred, and platinum being particularly preferred.

5 The invention further includes the method of removing carbon monoxide from a process fuel gas for a fuel cell via the utilization of a shift converter which employs the improved catalyst composition.

The foregoing and other features and advantages of the present invention will become more apparent in light of the following detailed description of exemplary
10 embodiments thereof as illustrated in the accompanying drawings.

Brief Description of Drawings

Fig. 1 is a simplified functional schematic diagram of a representative fuel cell power plant, depicting a shift converter employing the improved catalyst composition in accordance with the invention; and

15 Fig. 2 is a graph depicting plots of the shift conversion activity of the improved catalyst of the invention vs. that of the Cu/ZnO catalyst previously used.

Best Mode for Carrying out the Invention

Referring to Fig. 1, there is depicted in functional schematic form, a fuel cell power plant 10. The power plant 10 includes a fuel cell stack assembly 12 of
20 conventional design and construction, and a fuel processing subsystem which includes a reformer 14, a shift converter 16 and an optional selective oxidizer 18. The fuel processor converts a hydrocarbon fuel source into a hydrogen-rich stream of fuel which is supplied as the fuel to the fuel cell stack assembly 12. Typically, the hydrocarbon fuel source is a liquid, such as gasoline, or a gas, such as methane,
25 natural gas, or the like, and is supplied to the Fuel inlet 20 of reformer 14. Air and/or steam is supplied to the Air/Steam inlet 22 of reformer 14. The reformer 14 reacts hydrocarbon fuel and steam and/or air to reform the hydrocarbon (and steam) to yield hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂), and residual steam/water (H₂O), in a well known manner. However, to further reduce or minimize
30 the presence of carbon monoxide (CO) which otherwise "poisons" the anodes of the fuel cell stack assembly, and to increase the yield of hydrogen in the hydrogen-rich fuel source for the fuel stack assembly 12, the effluent process gas from the reformer

14 is conducted, via conduit 24, to the shift converter 16, where it is processed to reform the carbon monoxide to carbon dioxide.

The shift converter 16 carries out an exothermic shift reaction as noted in the formula (1) expressed in the Background Art above. The desired reaction in the shift
5 reactor 16 is the conversion of carbon monoxide and water to carbon dioxide and hydrogen. To the extent necessary, an optional selective oxidizer 18 may also be provided, and receives effluent process gas from the shift reactor 16 via conduit 26, to further convert carbon monoxide to carbon dioxide through the addition of air (O₂). The resultant effluent gas stream is sufficiently rich in hydrogen and depleted of
10 carbon monoxide to meet the needs of the fuel cell stack assembly 12, and is extended thereto via conduit 30.

The shift converter 16 includes a housing having a catalyst chamber 32 containing one or more catalyst beds or functionally equivalent structures, 34, for promoting the desired shift reaction. The process gas from the reformer 14 enters the
15 shift reactor 16 at inlet 36, flows through and across the catalyst bed(s) 34 in the catalyst chamber 32, and exits via outlet 38. Each catalyst bed 34 contains a catalyst composition, or simply, catalyst, 50, formulated particularly for improving the performance of the shift reactor 16 in accordance with the invention. Although the catalyst 50 is depicted here as a bed within the catalyst chamber 32, it will be
20 appreciated, that other arrangements for supporting the catalyst 50 within the catalyst chamber 32 are well known and are contemplated as alternatives. For instance, a preferred arrangement may be that of a honeycomb-type structure of ceramic, alumina, cordierite (alumina/magnesia/silica), or the like, mounted in the catalyst chamber 32 and containing the catalyst as a coating thereon.

25 The catalyst 50 is a formulation of a noble metal on a promoted support of mixed metal oxides, in which at least two of the metal oxides include cerium oxide, or ceria, (CeO₂) and zirconium oxide, or zirconia, (ZrO₂). The literature suggests that ceria acts to promote noble metal catalysts for the water-gas shift reaction, by serving as a source of oxygen vacancies. Increasing the oxygen vacancies is thought to
30 correspond to an improved water-gas shift reaction rate. Importantly, the addition of one or more additional metal oxides, of which an essential one is zirconia, to the ceria to create a mixed metal oxide promoted support (i.e., the support is a promoter) for the noble metal has been found to give the resulting catalyst composition 50 improved resistance to sintering at the higher operating temperatures (400 – 700⁰ F) (204 -

371°C) of the shift converter 16, as well as to further enhance the number of oxygen vacancies of the promoted catalyst.

The ceria and the zirconia are present in the catalyst composition in relation to one another in the range of about 50.0 to 30.0 mole% (mole per cent) zirconium to
 5 50.0 to 70.0 mole% (mole per cent) cerium. A third metal oxide may be present in the range of 0.0 to 10.0 mole% of the total oxide. The noble metal is in the range of 0.1 to 2.0 mole%, with 0.3 mole% being the value in a representative example. The quantity of zirconium should not be less than 30.0% in order to assure the enhanced stability it provides to the catalyst 50, nor should it be greater than 50.0% in order to prevent
 10 phases in the system which are only zirconia and/or only ceria.

An exemplary formulation of and for the catalyst composition 50 for shift reactor 16 is provided in the following Example, in which the MEI 01023 pellet material is a metal oxide mix of ceria and zirconia, and serves as the catalyst support for the noble metal catalyst. The noble metal catalyst is platinum. The ceria is present
 15 in the pellet in the amount of 58 mole% Ce, and the zirconia is present in the amount of 42 mole% Zr. The MEI 01023 is available from Magnesium Elektron Inc. of Flemington, New Jersey. The promoted support material, MEI 01023, of ceria and zirconia, was provided in the form of small pellets of 1/16 inch diameter, but might also have been provided as a powder or the like. The following Example uses the
 20 method of incipient wetness to apply the platinum to the supports. Other methods of adding the noble metal are well known.

EXAMPLE

Support	36.600 g pellets (50 cc)
25 Pore volume	0.700 g water/g catalyst
Amount of solution	25.620 g liquid solution containing Pt (see below) fills all the pores of the pellets
30 Amount of Pt	
Diamminodinitrite - 61%	
Pt (labeled)	0.247 Pt/Pt (NH ₃) ₂ (NO ₃) ₂
Pt Solution	
35 Pt(NH ₃) ₂ (NO ₂) ₂	0.247

DI water	15.372
Nitric Acid	10.248

Steps:

- 5 1. Weigh out and dry the pellet support (MEI 01023) for 2 hours at 212°F (100°C).
2. Dissolve $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ in 10.248 ml concentrated nitric acid as indicated, stirring constantly.
3. Once Pt dissolved, add Pt acid solution to the DI water.
4. Pour resulting solution over dried pellets, then stir with glass or Teflon® stirrer
- 10 until support is uniformly coated.
5. Dry resulting mixture for 1h at 212°F (100°C), then calcine 4h at 752° (400°C).
6. Weigh dried and calcined mixture to assure/determine complete mass balance.

This formulation uses pellets of the ceria and zirconia, and coats it with the platinum.

The resulting dried and calcined mixture represents the catalyst composition 50.

- 15 Alternatively, powders of the mixed metal oxide may be wash-coated onto an appropriate supporting substrate of alumina or cordierite, or such, and then the platinum can be applied to the wash-coated support in a manner similar to the preparation of the pellets. Further, it may be desirable to add alumina to the powder to improve its suitability for wash-coating onto a supporting substrate. The alumina
- 20 facilitates the adhesion of the wash-coat to the supporting substrate.

Fig. 2 is an Arrhenius plot showing the shift conversion activity of catalyst composition 50, prepared in accordance with the Example above, in graphic comparison with that of pellets of copper/zinc oxide catalyst of the type previously used as the catalyst in shift reactors for this water-gas shift reaction. The parameter

25 measured logarithmically along the y-axis is a reaction rate constant, k , at a given temperature, for the water-gas shift reaction. The parameter measured linearly along the x-axis is the inverse of the temperature at which reactivity is measured, or $1000/T$.

It is seen that the Cu/ZnO of the prior art increases the reaction rate at a 1st slope as the temperature increases from 300°F (149°C) to about 400°F (204°C), and there after

30 at a much lower 2nd slope as the temperature increases further from 400°F (204°C) to about 600°F (316°C). However, it will be noted that the Pt on $\text{CeO}_2/\text{ZrO}_2$ catalyst of the invention increases its reaction rate at a substantially constant slope, comparable to the 1st slope above, as the temperature increases from about 380°F (193°C) to 600°F (316°C). It will be observed that at the cross-over region of about 580°F (364°C) to

600°F (315°C), the catalyst composition of the invention exhibits activity that is equivalent to the activity of the Cu/ZnO. Thus, for such level of activity, a reactor utilizing the noble metal catalyst 50 of the invention would be approximately the same size as a reactor using the conventional Cu/ZnO catalyst, yet would not require
5 the additional cost, volume, and complexity of the reducing/purging/inerting system(s) presently associated with the latter. .

Although zirconia is the second metal oxide in the mix with ceria, further advantages, such as lower overall cost, may be derived by including a third metal oxide in a ternary mix of such oxides. The third metal oxide may conveniently be
10 selected from the group consisting of praseodymium oxide, lanthanum oxide, neodymium oxide, and hafnium oxide. The addition of one or more of these metal oxides serves to assist ZrO₂ in its stabilization and promotion of ceria.

The noble metal, or metals, that comprise(s) the catalyst supported by the mixed metal oxides of at least ceria and zirconia, is/are selected from the metals of
15 groups VIIb, VIII, and Ib of the second and third transition series of the periodic table. That group of noble metals includes rhenium, platinum, palladium, rhodium, ruthenium, osmium, iridium, silver, and gold. Platinum, palladium, rhodium, and/or gold, alone or in combination, are generally preferred, and platinum is the noble metal that is particularly preferred. Platinum is preferred because it provides the level of
20 activity required to obtain the desired reaction rate in a reactor of reasonable size/volume.

Claims

- 1 1. A shift converter (16) for reducing the amount of carbon monoxide in a
2 process gas (20, 24) using a water gas shift reaction, the shift converter (16) having a
3 catalyst chamber (32), the chamber (32) having an inlet (36) for entry of the process
4 gas into the chamber, an outlet (38) downstream of the inlet for exit of effluent from
5 the chamber, and a catalyst composition (50) located between the inlet (36) and the
6 outlet (38) for converting at least a portion of the carbon monoxide and water in the
7 process gas into carbon dioxide and hydrogen, the improvement wherein the catalyst
8 composition (50) in the catalyst chamber (32) comprises:
9 a noble metal catalyst having a promoted support, said promoted support
10 comprising a mixed metal oxide of at least cerium oxide (ceria) and zirconium oxide
11 (zirconia).
- 1 2. The shift converter (16) of claim 1 wherein, in the mixed metal oxide, the
2 amount of cerium present is in the range of 30 to 50 mole% and the amount of
3 zirconium present is in the range of 70 to 50 mole%.
- 1 3. The shift converter (16) of claim 1 wherein the noble metal of the catalyst
2 composition (50) is selected from the group consisting of platinum, palladium,
3 rhodium, and gold.
- 1 4. The shift converter (16) of claim 3 wherein the noble metal of the catalyst
2 composition (50) is platinum.
- 1 5. The shift converter (16) of claim 1 wherein the metal oxide comprising the
2 promoted support additionally includes at least a third metal oxide.
- 1 6. The shift converter (16) of claim 5 wherein the third metal oxide is selected
2 from the group consisting of praseodymium oxide, lanthanum oxide, neodymium
3 oxide, and hafnium oxide.

1 7. The shift converter (16) of claim 1 wherein at least the promoted support of
2 the catalyst composition (50) is wash-coated onto a supporting substrate, and further
3 including alumina mixed with the promoted support to facilitate adhesion of the
4 wash-coat onto the supporting substrate.

1 8. The shift converter (16) of claim 1 wherein the catalyst composition (50)
2 operates independent of any requirement for prereduction, a shutdown purge, or an
3 inerting atmosphere.

1 9. The shift converter (16) of claim 1 wherein the shift converter (16) is
2 operatively connected in a fuel processing subsystem (14, 16, 18) for a fuel cell (12).

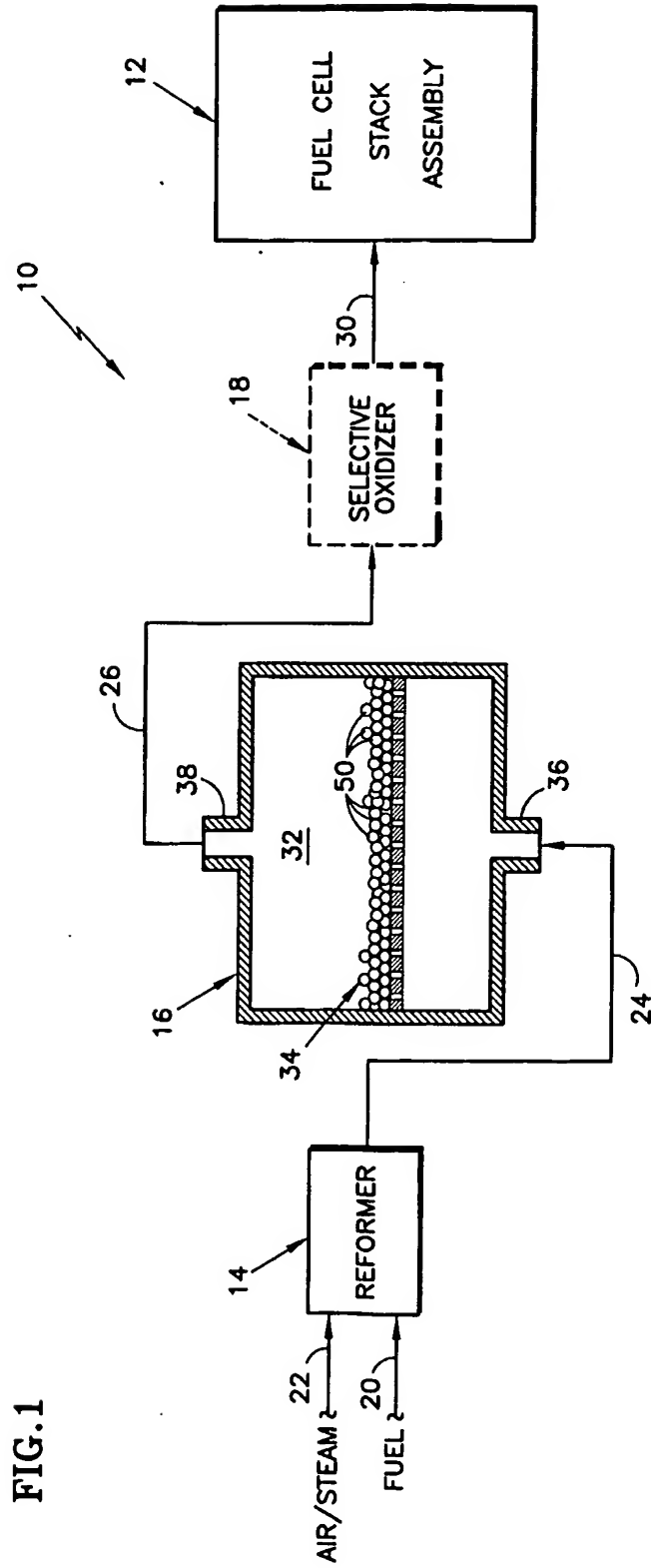
1 10. The shift converter (16) of claim 8 wherein the shift converter (16) is
2 operatively connected in a fuel processing subsystem (14, 16, 18) for a fuel cell (12)
3 and the process gas includes hydrogen.

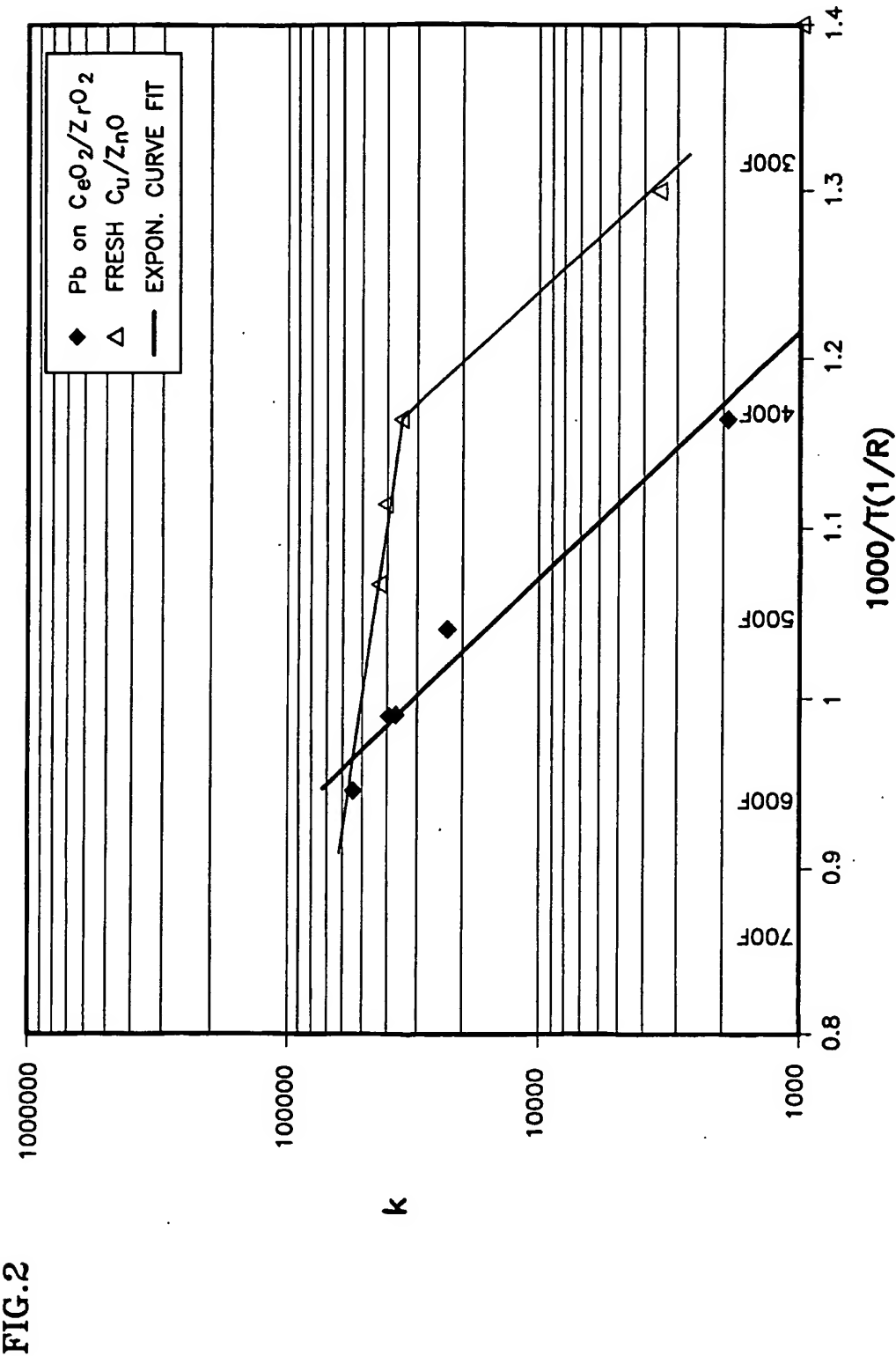
1 11. The method of reducing the amount of carbon monoxide in a process fuel gas
2 for a fuel cell (12), comprising the steps of:

- 3 a. placing a catalyst composition (50) of a noble metal catalyst having a
4 promoted support into a shift converter (16), the promoted support comprising a
5 mixed metal oxide of at least cerium oxide and zirconium oxide; and
6 b. passing the process fuel gas into operative proximity with the catalyst
7 composition (50) to convert at least a portion of the carbon monoxide in the process
8 fuel gas into carbon dioxide and hydrogen via a water-gas shift reaction.

1 12. The method of claim 11 wherein the catalyst composition (50) obviates any
2 requirement for prereduction, a shutdown purge, or an inerting atmosphere, in
3 association with the operation of the shift converter (16).

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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US CL : 422/211; 423/655, 656

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 422/211; 423/655, 656

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
 NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 DERWENT**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y — A	US 5073,532 A (DOMESLE ET AL) 17 December 1991 (17.12.91), see col. 1, line 48 to col. 2, line 68.	2,5-7 — 9-101
X — Y — A	US, 6040,265 A (NUNAN) 21 March 2000 (21.03.00), see col. 1, line 14 to col. 4, line 65.	1, 3, 4, 8 — 2, 5-7 — 9-10
A	US 5,830,425 A (SCHNEIDER ET AL) 03 November 1998 (03.11.98), see col. 2, line 55 to col. 5, line 59.	1-11

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family
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Date of the actual completion of the international search

10 AUGUST 2002

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/12972

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, 5,039,503 A (SAUVION ET AL) 13 August 1991 (13.08.91), see col. 1, line 6 to col. 2, line 49.	1-11
A	US 5,990,040 A (HU ET AL) 23 November 1999 (23.11.99), see col. 4, line 45 to col. 7, line 17.	1-11
A	US 4,835,132 A (SAMBROOK) 30 May 1989 (30.05.89), see col. 1, line 5 to col. 4, line 20.	1-11